

1,189,304

# PATENT SPECIFICATION



NO DRAWINGS

1,189,304

Inventors: KEITH GEORGE ALLUM and ERIC SIMON FORBES

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## COMPLETE SPECIFICATION

### New Sulphur-Containing Phosphonate Esters and Lubricating Compositions containing them

We, THE BRITISH PETROLEUM COMPANY LIMITED, of Britannic House, Moor Lane, London, E.C.2, England, a company incorporated in accordance with the Laws of

5 England, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

10 This invention relates to a new class of load-carrying lubricating oil additives and their use in lubricating oils, more particularly it relates to load-carrying compounds containing both phosphorus and disulphide groups.

15 It is generally considered that load-carrying additives may be divided into two classes, namely antiwear and extreme pressure additives. When two lubricated moving surfaces are lightly loaded against each other,

20 they are separated by an elasto-hydrodynamic oil film: as the load increases so the oil film thickness decreases. When the oil film thickness approaches the dimensions of the surface roughness, it will be penetrated by surface

25 asperities: it is in this region that antiwear additives function by improving the oil film strength and thus reducing intermetallic contact. As the load is increased further, the bulk oil film collapses and antiwear additives are no longer sufficient to protect the surface.

30 Extreme pressure additives function in this region by reacting with the metal surface to form an inorganic iron compound, such as iron sulphide, which prevents welding of the metal surfaces.

35 A useful source of information on this subject, with particular reference to disulphides, may be found in an article in the *Journal of the Institute of Petroleum*, Vol.

40 15, No. 497, pp. 145—161, May 1965. Further relevant information on this subject may be found in our co-pending Application No.

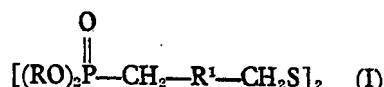
36723/64 (Serial No. 1043788) (extreme pressure additives) and No. 31248/65 (Serial No. 1135224) (anti-wear additives).

45 It is also known that phosphorus compounds, for example, phosphonates and phosphates, are useful as anti-wear additives. A useful source of information on this subject is a Thesis by Klaus, E. E., Pennsylvania State College, 1952.

50 It is generally considered that anti-wear additives act by chemisorption on the surfaces of metals, whereas extreme pressure additives act by reaction with the metal surface. It is also known that phosphorus compounds are, in general, good anti-wear additives, whereas sulphur compounds, particularly some disulphide compounds, are good extreme pressure additives. It is also known that mixtures of good anti-wear additives and extreme pressure additives often do not retain their activity over the anti-wear and extreme pressure regions. See, for example, the report on the Third Convention on Lubrication and Wear, 27th—28th May, 1965, London. Paper 17 by Barcroft, F. T., and Deniel, S. G., particularly pp. 122, 123). The reaction mechanisms are complex and certainly not well understood.

55 It was, therefore, quite unexpected to discover that both anti-wear and extreme pressure properties could be provided in a single additive.

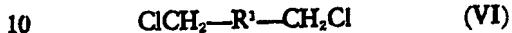
60 According to the invention, a novel additive having both anti-wear and extreme pressure properties is provided, which has the general formula



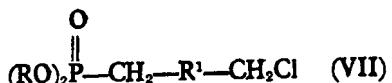
65 wherein R is an alkyl, aryl, aralkyl, alkaryl or cycloalkyl group having up to 20 carbon atoms, 80

and R<sup>1</sup> is a vinylene or phenylene group which is unsubstituted or is substituted with a C<sub>1-10</sub> alkyl group, preferably R is a C<sub>1-4</sub> alkyl group.

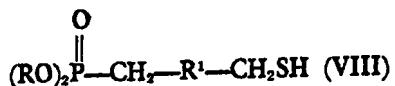
5 This invention also relates to a method of preparing a compound of general formula (I) herein which comprises reacting a phosphite of general formula (RO)<sub>2</sub>P (V) with a dichloro compound of general formula



to form a compound of general formula



15 and then reacting compound (VII) with an alkali metal hydrosulphide to form a compound of general formula



20 and then oxidising the compound of general formula (VIII) to form a compound of general formula (I). Preferably the reaction between compounds (V) and (VI) is carried out at a temperature of between 150 and 165°C and the preferred oxidising agent is a solution of iodine in potassium iodide and sodium bicarbonate solution.

This invention further relates to a lubricating compositions containing these additives in an amount of up to 100 millimoles per 100g. of blend, preferably from 0.01 to 20 millimoles.

In a particularly preferred embodiment of the invention the group R<sup>1</sup> is unsubstituted vinylene and the groups R are ethyl or butyl.

The extreme pressure properties of the blends were assessed by means of the four-ball EP test. This method comprises loading a rotating steel ball against a triangle of stationary steel balls in a bath of the blend. A series of tests are carried out over a range of loads until welding of the balls occurs. The results of the test are expressed in terms of the Mean Hertz Load, 2½ second seizure delay load, welding load and initial seizure load. The four-ball test and method of obtaining the results above is described in method 6503 of the US Federal Test Method Standard Number 791a. The figures quoted in this specification, however, were obtained using a 60 second test period instead of the 10 second test period described in the Federal Test Method.

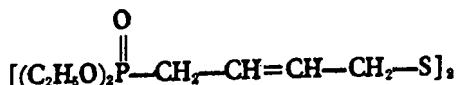
40 The antiwear properties of the blends were assessed by running the four-ball machine at 50°C under a load of 15 kg and measuring the wear scars on the balls after 30, 45 and 60 minutes.

45 The invention will now be particularly described by reference to an Example.

#### EXAMPLE

Di[4,4<sup>1</sup>-(diethyl phosphono-) but-2-enyl] disulphide

60



Formula II

was prepared as follows:

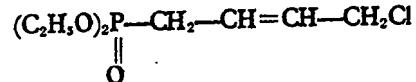
Triethyl phosphite,



65 (1 mole), was added to an excess of 1,4-dichloro-but-2-ene,



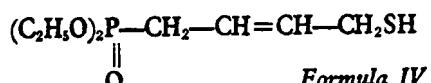
(3 moles), at 80°C and heated at 150°C to 70 165°C for 3 hours. Ethyl chloride was generated during the reaction. Distillation yielded 4-(diethyl phosphono)-1-chloro-but-2-ene:



(b.p. 92°—94°C at 0.2 mm mercury).

Formula III

This compound (1 mole) was dissolved in ethanol and a cold solution of sodium hydrosulphide (> 1 mole, prepared from EtONa and H<sub>2</sub>S at -10°C) in ethanol was added. The solution produced was stirred for 2 hours at room temperature and then filtered. After removal of the ethanol, the residue was extracted with ether and the extra filtered, dried and distilled to give the compound 1-mercaptop - 4 - (diethyl phosphono)but - 2-ene:



Formula IV

(b.p. 98°—100°C at 0.1mm mercury)

80 85 This compound was oxidised to the disulphide (of Formula II) by dissolution in aqueous sodium bicarbonate solution at 5°C and the slow addition of a cold solution of

- iodine in potassium iodide ( $K^+I^-$ ). The product was extracted with ether, dried and the solvent removed to yield a pale yellow oil which was purified by deposition from ether/petroleum ether solution at  $-70^\circ C$ .  
Elemental analysis, infra red and nuclear magnetic resonance spectroscopy confirmed that the product was as represented by Formula II.
- Anti-wear and extreme pressure results, as measured using the four-ball tester, are shown in the attached Table.

TABLE

Composition	Conc. of additive in millimoles % per 100 g of blend	Anti-wear test			Extreme pressure test		
		30 min.	45 min.	60 min.	Mean Hertz Load (kg)	Initial Seizure Load (kg)	2½ sec. Seizure Delay Load (kg)
1. Di-iso-octyl sebacate	—	0.66	0.75	0.81	16.2	45	47
2. Liquid paraffin	—	0.60	0.72	0.78	13.5	45	45—50
3. $\text{O} \begin{array}{l} \parallel \\ \text{(EtO)}_2\text{P}-n-\text{Bu} \end{array} \text{I}_{12}$	4.63	0.56	0.58	0.64	—	—	—
4. $\text{O} \begin{array}{l} \parallel \\ \text{(EtO)}_2\text{P}-\text{CH}_2-\text{Ph} \end{array} \text{I}_{12}$	4.63	0.40	0.41	0.45	—	—	—
5. $\text{O} \begin{array}{l} \parallel \\ \text{(EtO)}_2\text{P}-\text{CH}_2-\text{CH}=\text{CH}_2 \end{array} \text{I}^2$	4.63	0.43	0.43	0.41	17.2	50	45—50
6. $\text{O} \begin{array}{l} \parallel \\ \text{(EtO)}_2\text{P}-\text{CH}_2-\text{CH}=\text{CH}_2 \end{array} \text{I}^2$	18.52	—	—	—	22.1	55	55—60
7. Compound of Formula II	2.32	0.39	0.40	0.42	31.7	80	78
8. Compound of Formula II	9.26	—	—	—	39.4	100	98
9. $\text{O} \begin{array}{l} \parallel \\ \text{[(EtO)}_2\text{P}-\text{CH}_2\text{CH}_2\text{S}]_2 \end{array}$	2.32	0.38	0.48	0.59	21.5	77	135
10. $\text{O} \begin{array}{l} \parallel \\ \text{[(EtO)}_2\text{P}-\text{CH}_2\text{CH}_2\text{S}]_2 \end{array}$	9.26	—	—	—	31.3	95	105
11. Diallyl disulphide	2.32	0.56	0.62	0.66	37.7	55	62
12. Diallyl disulphide	9.26	—	—	—	60.0	70	70—80

All the compounds were tested in di-isooctyl sebacate base oil except the compounds marked<sup>1</sup> which were tested in liquid paraffin.

<sup>2</sup>The phosphonates were blended to give oils 5 containing the same per cent weight phosphorus as those blends containing the compound of Formula II with which they are compared.

From this Table it can be seen that the 10 compound of Formula II has equivalent anti-wear properties to diethyl allyl phosphonate (which has good anti-wear properties) and although the extreme pressure properties of the compound according to the invention are almost equivalent to those of diallyl disulphide 15 they are considerably better than those of diethyl allyl phosphonate. The compound of Formula II has also considerably better anti-wear properties than diallyl disulphide.

20 It can also be seen that a compound containing an allylic carbon to sulphur bond and an allylic carbon to phosphorus bond in the same molecule is superior in both anti-wear and extreme pressure properties to a compound such as:

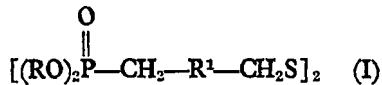


An increase in concentration does not effect 30 the superiority of the compound of Formula II over diethyl allyl phosphonate or the compound of Formula IX, in the extreme pressure region. Results at higher concentrations in the anti-wear region have not been submitted because the effect of change in concentration on anti-wear performance is not 35 straightforward for some compounds (see our co-pending Application No. 31248/65 (Serial No. 1135224)).

To summarise, it can be seen from this 40 Table that the presence of an unsaturated group, for example, a vinylene or phenylene group, in a beta-position to both a phosphorus atom and a sulphur atom contained in the same molecule, promotes both high anti-wear activity and high extreme pressure activity in 45 the molecule.

#### WHAT WE CLAIM IS:—

##### 1. Compounds of the general formula



50 where R is an alkyl, aryl, cycloalkyl, alkaryl, or aralkyl group, having up to 20 carbon atoms, and R<sup>1</sup> is a vinylene or phenylene

group which is unsubstituted or is substituted with a C<sub>1-10</sub> alkyl group.

2. A compound as claimed in claim 1 in which R is a C<sub>1-4</sub> alkyl group. 55

3. A compound as claimed in claim 1 in which R<sup>1</sup> is unsubstituted vinylene and R is ethyl or butyl.

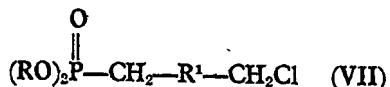
4. A method of preparing compounds of general formula (I) herein which comprises reacting a phosphite of general formula 60



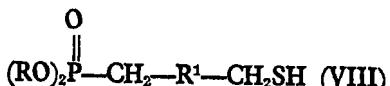
with a dichloro compound of general formula



to form a compound of general formula 65



and then reacting compound (VII) with an alkali metal hydrosulphide to form a compound of general formula



70 and then oxidising the compound of general formula (VIII) to a compound of general formula (I).

5. A method as claimed in claim 4 in which the reaction between the compounds of general formula (V) and (VI) is carried out at a temperature of between 150°C and 165°C. 75

6. A method as claimed in claim 4 or 5 in which the oxidation of the compound of general formula (VIII) is carried out by the reaction of the compound of formula (VIII) with a solution of iodine in the presence of potassium iodide and sodium bicarbonate. 80

7. A method of preparing compounds of general formula (I) herein, as herein before described with reference to the Example. 85

8. Compounds of general formula (I) when prepared by the method of any one of claims 4-7. 90

9. A lubricating composition which contains up to 100 millimoles per 100 grams of the composition of a compound claimed in any one of claims 1-3 or 8. 95

10. A lubricating composition as claimed in claim 9 which contains from 0.01 to 20 millimoles of a compound claimed in any one of claims 1-3 or 8.

J. WOOLARD,  
Agent for the Applicants.  
Chartered Patent Agent.